Sandia's Flow Battery Membrane Development

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DOE Office of Electricity Program Merit Review

October 26 – 28th 2021

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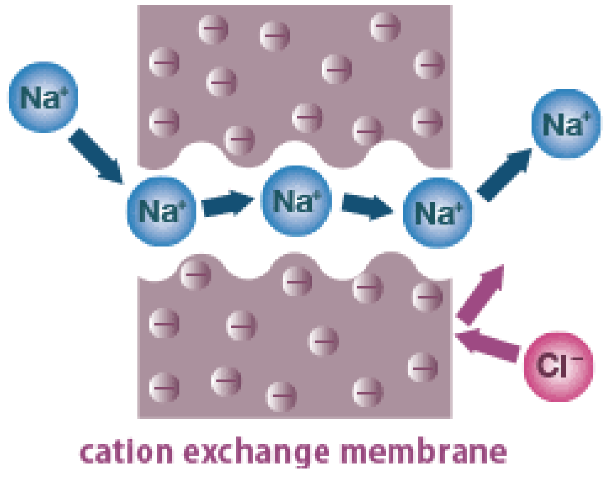
Membrane Basics

Objective: To develop membranes for flow batteries to lower cost and improve performance which will facilitate commercialization.

- *Cost: Developing hydrocarbon based membranes.*
- *Performance: Membrane conductivity determines battery resistance and membrane selectivity regulates capacity retention.*



Typically used in acidic environments, but recent work is employing membrane at high pH

- **Focus: Most commercial interest still lies in cation exchange membrane; PFSA replacement (e.g. Nafion).**

Licensed Membrane Patents

1. XERGY

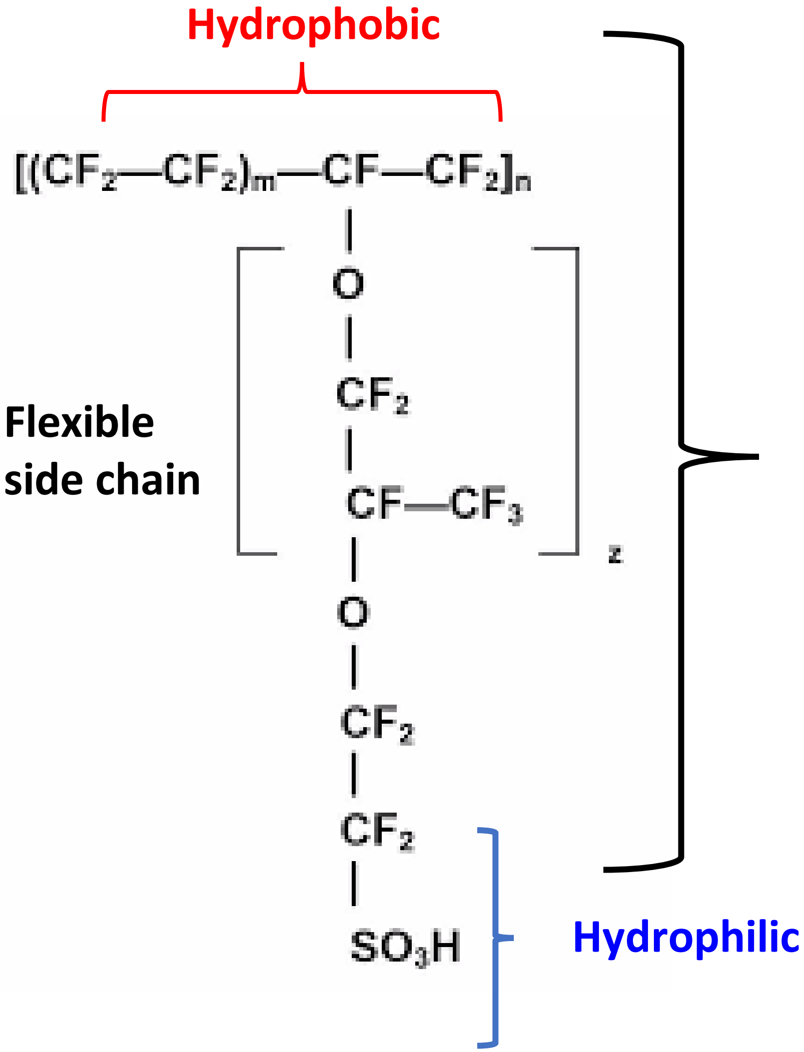
May 2021, Xergy Inc. a Delaware based material company, **renewed** non exclusive licenses of several patents that were developed in the OE program. Discussions are now around commercial license.

1) U.S. Patent No. 7,301,002, entitled Sulfonated Polyphenylene Polymers, issued on November 27, 2007. (SD#7565.1)
2) U.S. Patent No. 9,580,541, entitled High Performance, Durable Polymers Including Poly(Phenylene), issued on February 28, 2017. (SD# 12691.1)
3) U.S. Patent No. 7,888,397, entitled Polyphenylene Based Anion Exchange Membrane, issued on February 15, 2011. (SD# 10987.0)
4) U.S. Patent No. 8,809,483, entitled Functionalization of Polyphenylene by Attachment of Sidechains, issued on August 19, 2014 (SD# 12299.0)
5) U.S. Patent No. 10,053, 534, entitled Functionalization of Diels-Alder Polyphenylene, issued on August 21, 2018 (SD#13592.1)
6) U.S. Patent No. 10,442,887, entitled Functionalization of Diels-Alder Polyphenylene, issued on October 15, 2019 (SD#13592.5)
7) U.S. Patent No. 10,294,325, entitled Halo Containing Anion Exchange Membranes & Methods Thereof, issued on May 21, 2019 (SD#14264.0)

2. Currently, a very large engineering company is looking into licensing membrane IP that was developed last year.

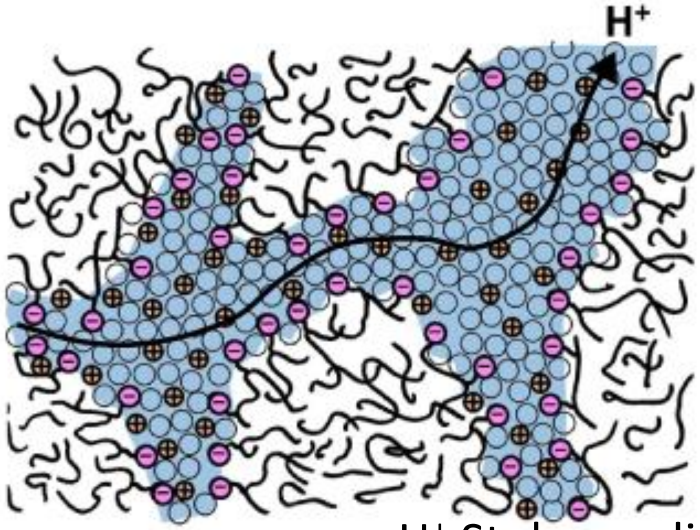
1) C. Fujimoto “Ion-Selective Membrane for Redox Flow Batteries” Non-provisional U.S. Patent Application No. 17/391,508, August 2, 2021.

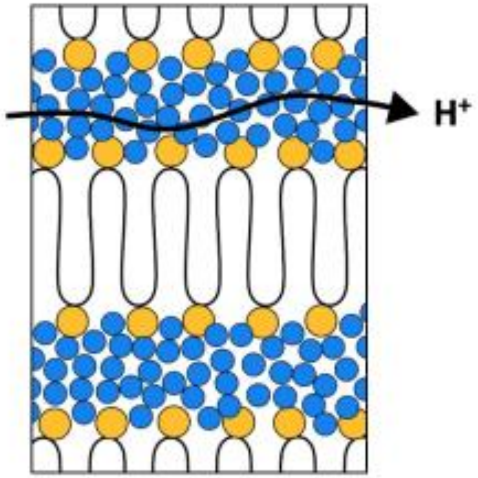
Relationship between ion transport and polymer structure



IEC = mmole SO_3H per gram of polymer

- Nafion has very high ionic conductivity and very good chemical stability. Issue is low ion selectivity.
- Polymer composition and structure plays a vital role in materials property!
- Polymer composition has two opposing physical features
- C-F bond highly hydrophobic
- SO_3H group highly hydrophilic
- Two opposing properties but held together by physical bond. When Nafion is in contact with water a phase separation occurs.

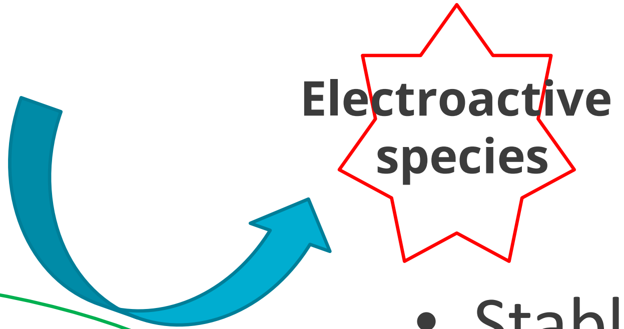


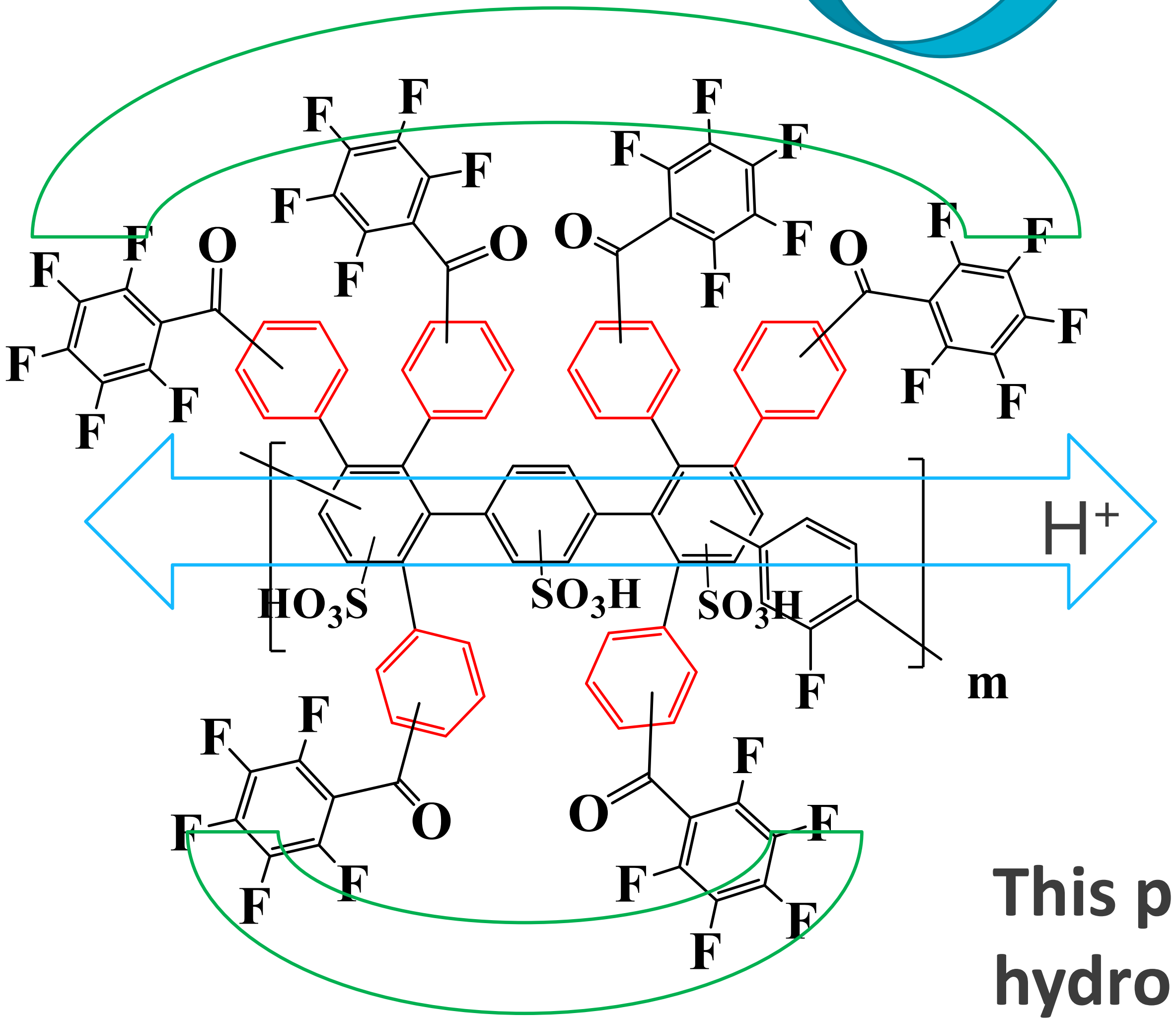


H^+ Stokes radius = 0.026 nm

V Stokes radius = 0.6 nm

Relationship between ion transport and polymer structure



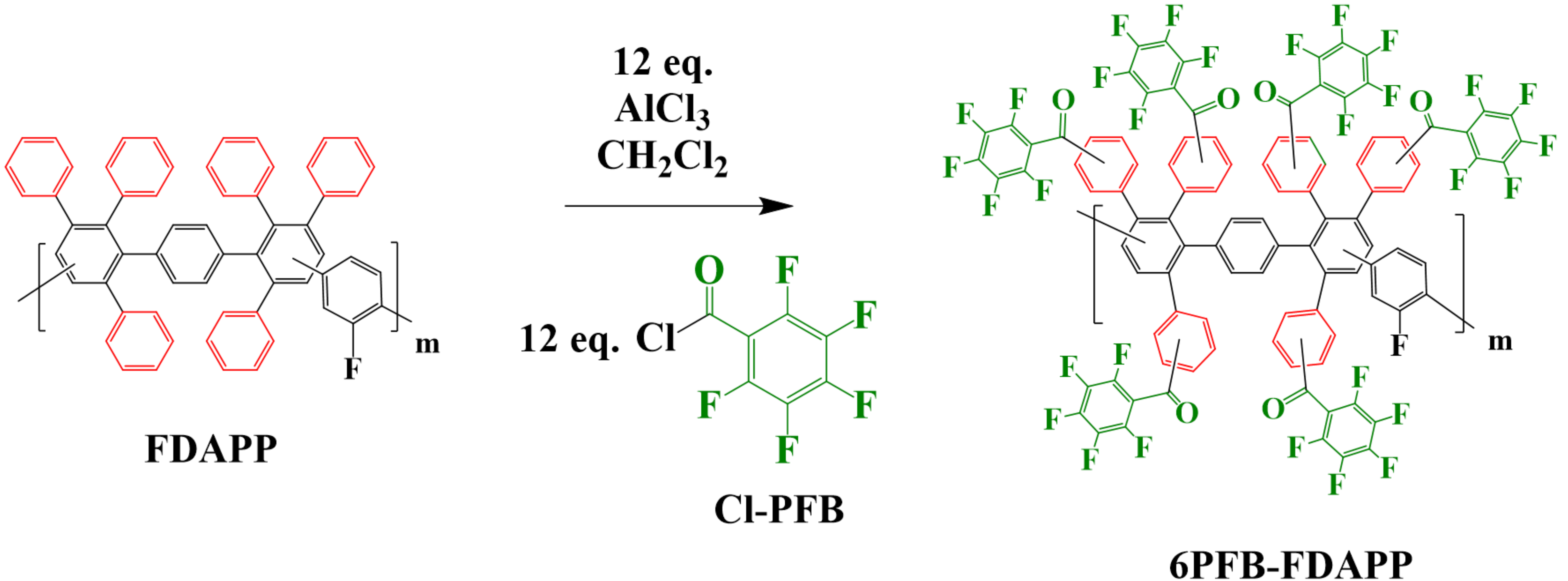


- Stable poly(phenylene) backbone. Two types of phenyls; pendant (red) backbone (black)
- Attach pentafluorobenzoyl group on to pendant phenyl; hydrophobic shell
- Attach sulfonic acid group on to backbone phenyl; hydrophilic core

This polymer structure will prevent large hydrophilic aggregation

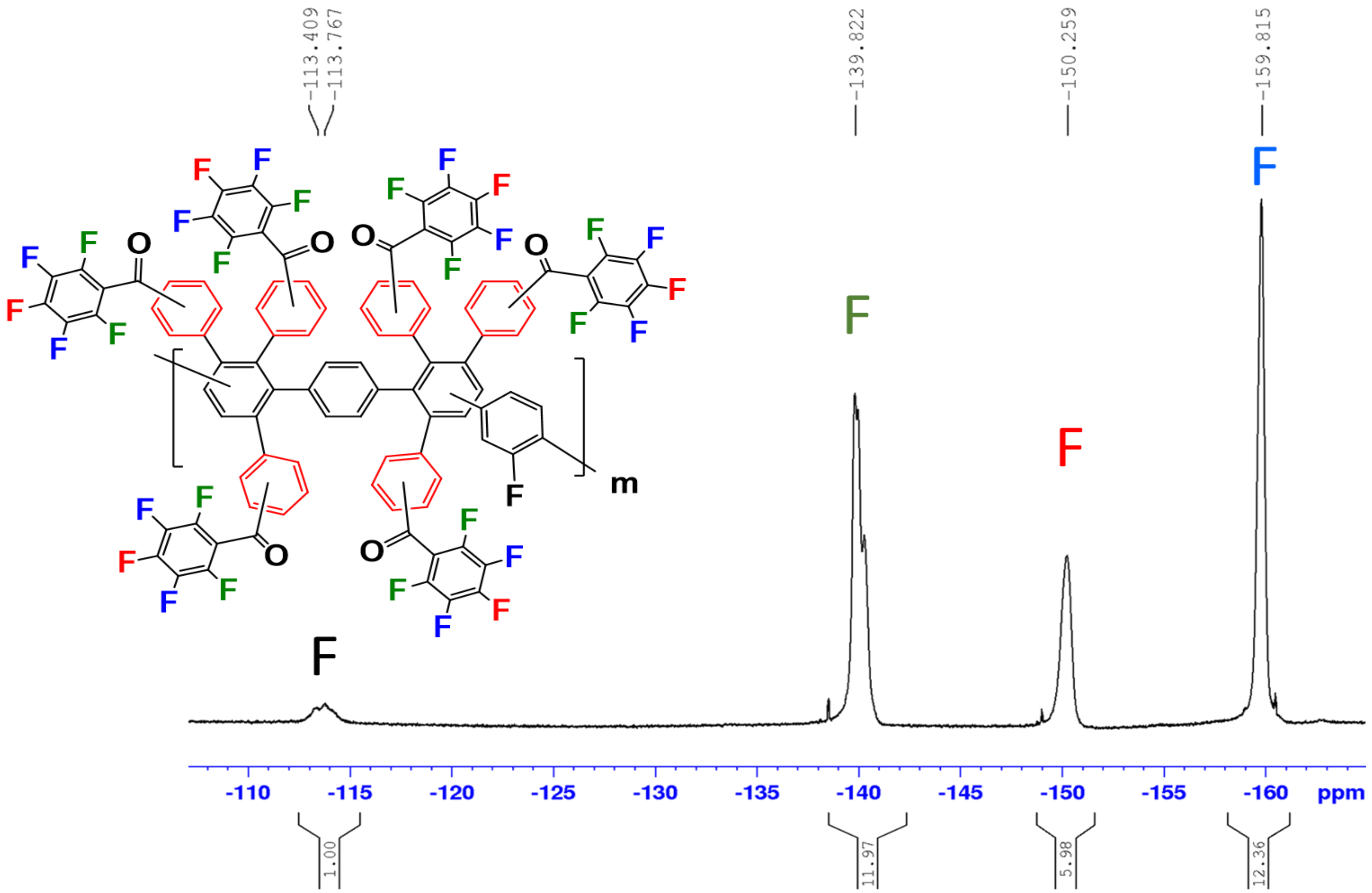
Synthesis step 1 of 2: 6PFB-FDAPP

Friedel Crafts Benzoylation



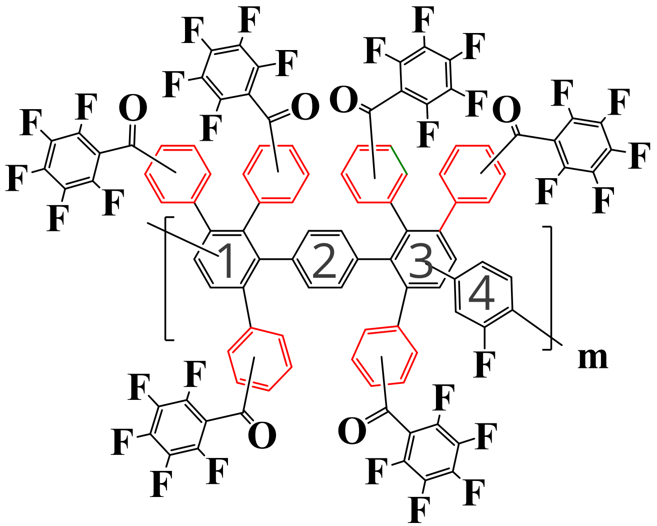
How do we know how many PFB (pentafluorobenzoyl) groups are attached?

Characterization of 6PFB-FDAPP: ^{19}F-NMR



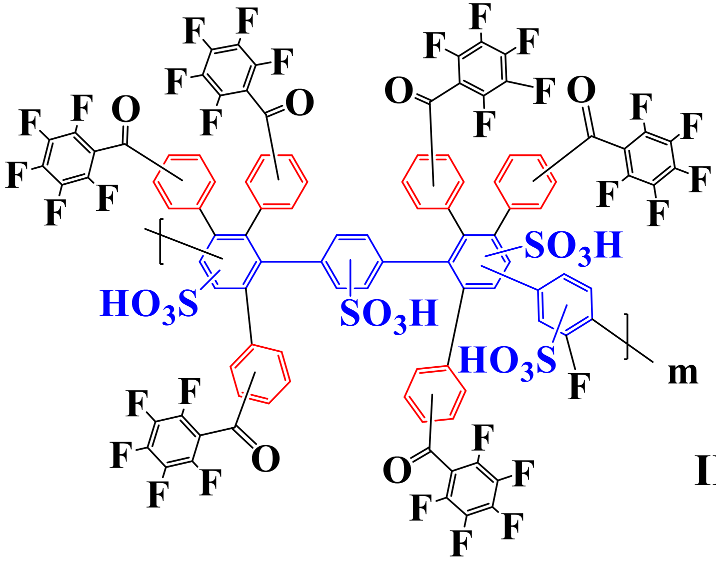
Synthesis step 2 of 2: S 6PFB-FDAPP

Friedel Crafts Benzoylation



6PFB-FDAPP

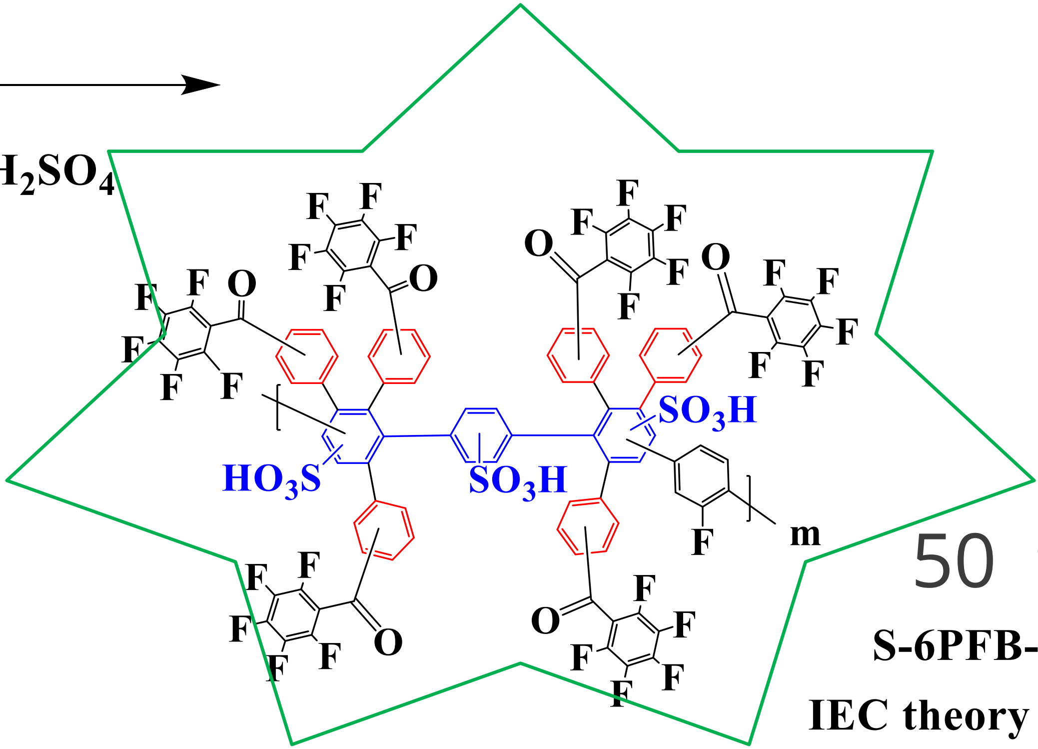
$\xrightarrow{H_2SO_4}$



65 °C

SS-6PFB-FDAPP

IEC theory 1.74 meq/g



50 °C

S-6PFB-FDAPP

IEC theory 1.35 meq/g

Energy Storage Grand Challenge; applications with SNL membrane

There is tremendous interest and investment in energy storage. In September, DOE awarded new projects and the leads from two of these new programs are currently evaluating the Sandia membrane.

Quino Energy, Inc. and partners (Menlo Park, CA) will receive $4.58 million to strengthen the U.S. domestic flow battery manufacturing ecosystem by developing and executing a scalable, cost-effective, and continuous process for producing aqueous organic flow battery reactants.

→ Professor Michael Aziz from Harvard University

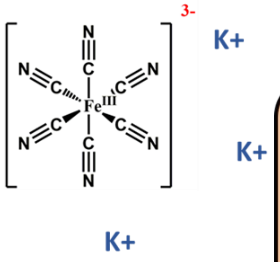
OTORO Energy Inc. and partners (Broomfield, CO) will receive $4.14 million to improve the cost, scalability, and performance of existing flow battery technology through a metal chelate flow battery system.

→ Professor Michael Marshak from UCB

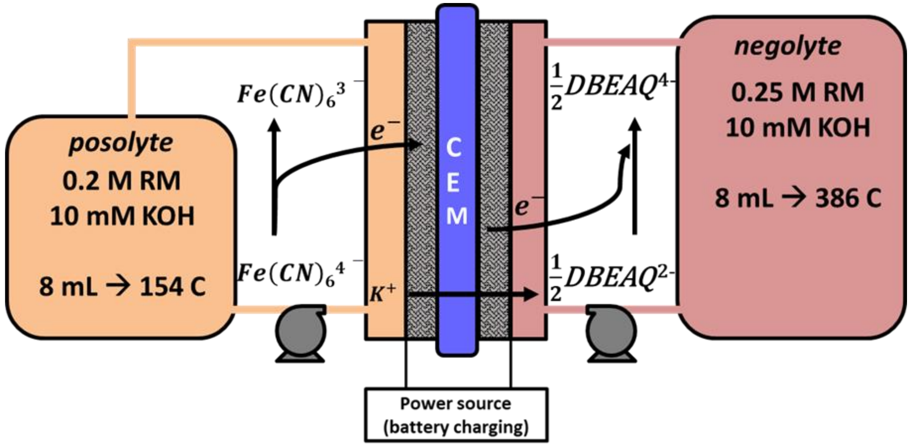
S-6PFB-FDAPP in Aqueous organic flow battery

Professor Michael Aziz at Harvard University

Tommy George and Zhijang Tang



Potassium ferricyanide



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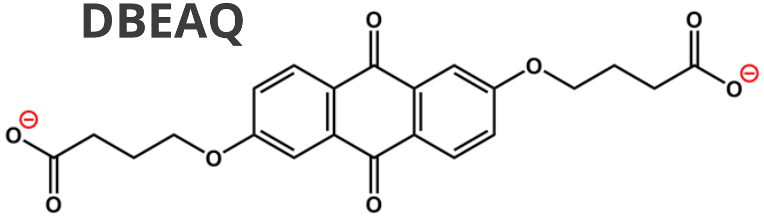
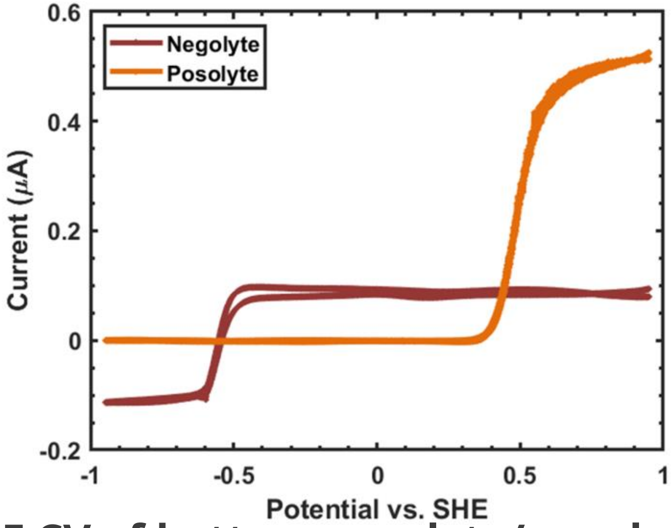


HARVARD
School of Engineering and Applied Sciences

Membrane Targets: 1. $D_{K_3[Fe(CN)_6]} < 1x10^{-11}$ cm^2 s^{-1} **2.** ASR < 1 ohm cm^2
3. Fade rate < 0.01% day^{-1}

Membrane	Diffusion cm^2 s^{-1}	ASR ohm cm^2	Fade rate % day^{-1}
N212	$3.4x10^{-12}$	4.1	0.53
S6PFB-FDAPP	$3.1x10^{-12}$	1.1	0.51



UME CV of battery posolyte/negolyte after 10 days cycling, no detectable crossover

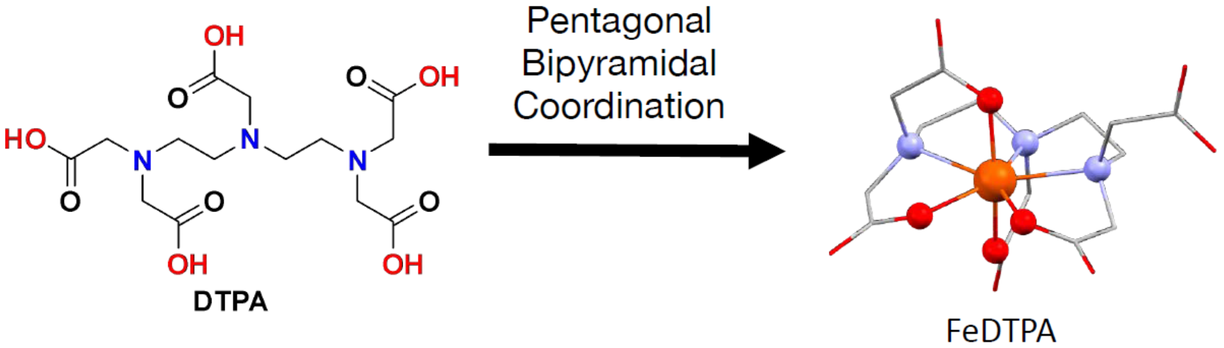
S-6PFB-FDAPP in Fe-Cr chelate flow battery

Professor Michael Marshak at UC Boulder

University of Colorado Boulder

Aminopolycarboxylate chelate in Fe-Cr redox flow battery

- Chelate improve metal solubility
- Increases metal size (reduce crossover)
- Chelate can manipulate redox potential
- Chelate found to improve redox reaction rates
- Low cost



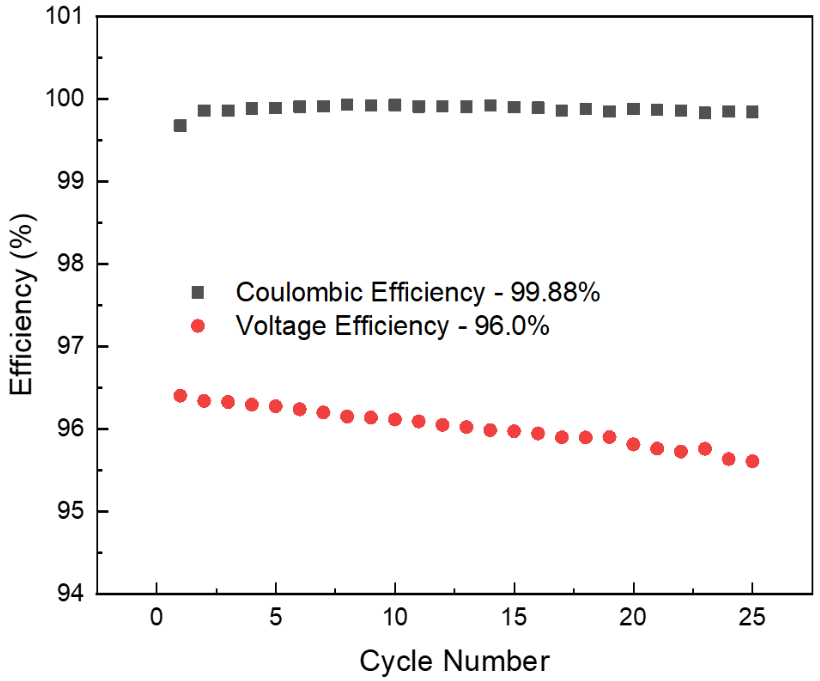
Brian Robb

Membrane	Thickness	Cell ASR	H-Cell Crossover (µA cm^{-2})		
			$K_4Fe(CN)_6$	$K_3Fe(CN)_6$	KCrPDTA
Nafion 212	50	1.48	2.4 (1-week)	2.9 (1-week)	8.3
Sandia 40	40	1.28	0 (3 weeks)	0 (3 weeks)	0 (3 weeks)
Sandia 20	20	0.99	0 (ongoing)	0 (ongoing)	0 (ongoing)

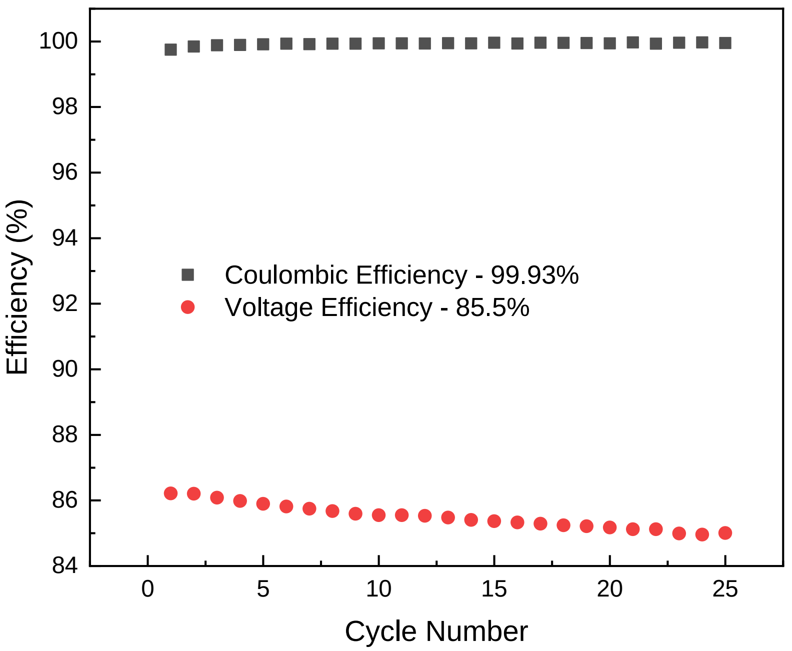
S-6PFB-FDAPP in Fe-Cr chelate flow battery

1 M KCrPDTA, 0.1 M KBi with a posolyte of 0.5 M $K_4Fe(CN)_6$/0.1 M $K_3Fe(CN)_6$, 0.1 M KBi at pH 9.

Membrane	Thickness µm	CE %	VE %	EE %	Avg. discharge $mW\ cm^{-2}$	Cell ASR $\Omega\ cm^2$
Nafion 212	50	99.5	79.3	78.8	141.1	1.48[b]
Sandia[d] 40	40	99.8	84.1	83.9	146.0	1.28
Sandia[d] 20	20	99.9	85.5	85.4	146.5	0.99



25 cycles – charging discharging at 20 mA/cm^2 to 80% SOC



25 cycles – charging discharging at 100 mA/cm^2 to 80% SOC

University of Colorado Boulder

Conclusions

- Seven membrane patents re-licensed (R&D) currently in discussion for commercial license.
- Introduce novel polymer structure to promote ion selectivity.
- In aqueous organic flow battery SNL membrane 4x lower resistance than Nafion.
- In aqueous metal complex flow battery lower membrane resistance (than Nafion) and no detectable electroactive species crossover.

Future Tasks

- Work with Professor Aziz's group to understand/minimize the cause of capacity loss.
- Work with Professor Marshak's group to reduce voltage losses through electroosmosis.

Patent and Paper

- C. Fujimoto "Ion-Selective Membrane for Redox Flow Batteries" Non-provisional U.S. Patent Application No. 17/391,508, August 2, 2021.
- M. Sandip "Durable and highly selective ion transport of a sulfonated Diels Alder Poly(phenylene) for vanadium redox flow batteries" Submitted to J. Power Sources.

Beyond Membranes: Redox Flow-Based Batteries (RFBs) at Sandia

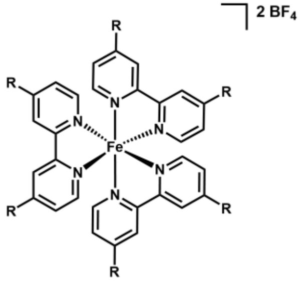
Travis Anderson (Non-Aqueous RFBs)

Harry Pratt
Claudina Cammack
Randi Poirier
Eric Deichmann
Reed Wittman (Yuilia Preger)

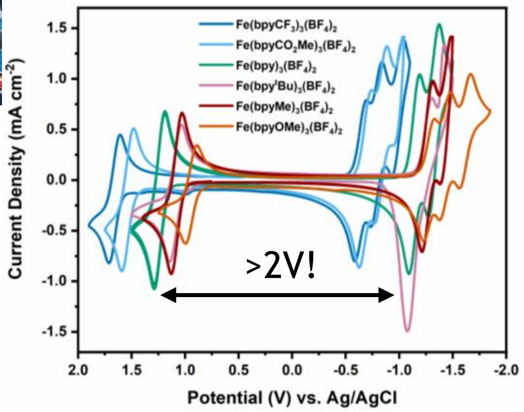
Rangachary Mukundun

Los Alamos NATIONAL LABORATORY EST. 1943

NA-RFBs *promise higher voltage batteries for increased energy density!*



Cammack, et al. Dalton Trans., 2021, 50, 858

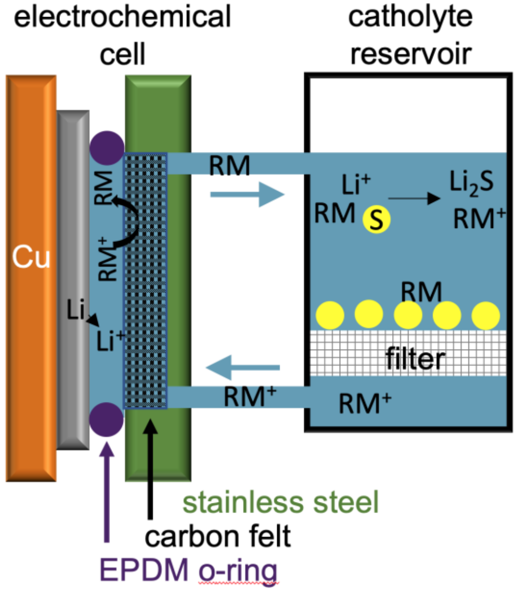


RFB University Collaborations:

UNC CHARLOTTE
UNIVERSITY of ROCHESTER
DAVIDSON
THE UNIVERSITY of NEW MEXICO
THE UNIVERSITY OF TENNESSEE KNOXVILLE
HARVARD UNIVERSITY
University of Colorado Boulder

Leo Small (Mediated Li-S)

Melissa Meyerson



Anode: Li-metal

Cathode: Sulfur

Ion-Selective Separator: None

Enabling Technology: Redox Mediators in Electrolyte

Mediated Li-S *has potential for high energy density, long-duration energy storage applications!*

Poster Presentation: "Metal Coordination Complexes for Symmetric, Non-aqueous Flow Batteries"

Poster Presentation: "Mediated Lithium-Sulfur Flow Batteries"

Thank You

We would like to gratefully acknowledge support from Dr. Imre Gyuk, Director of the Energy Storage Research Program in the U.S. Department of Energy Office of Electricity.

Questions?

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